

Synthetic Organic Chemicals

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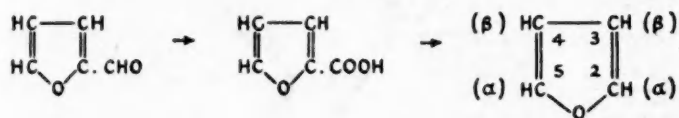
Some Metallic Compounds of Furan

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OF INTEREST from the historical standpoint is the fact that Scheele described a derivative of furan more than fifty years before the isolation and study of benzene laid the foundations of aromatic chemistry. In spite of this historical priority, the chemistry of furan and its derivatives was, for many years, a relatively neglected field. Recently, however, the study of furan, furfural, and furfuryl alcohol has received impetus from the fact that there is an immense potential source of these materials in agricultural products.

Furan is readily prepared by decarboxylation of pyromucic acid which is obtained by the oxidation of furfural:



Furan shares with its analogues, pyrrole and thiophene, the property of escaping the application of Korner's absolute method for establishing orientation of nuclear substituents. This fact (the reasons for which are pointed out by Gilman, *CHEM. REV.*, 11, 323, 1932) has resulted in confusion in proving the structure of some of the simplest of the derivatives of furan, such as nitrofuran. One of the classical methods for estab-

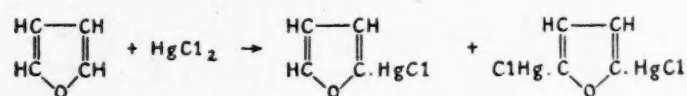
lishing orientation in the furan nucleus has involved ring-scission by treatment with acid or alkali, followed by a study of the aliphatic compounds thus produced. In recent years, the problem of orientation in furan has been completely solved insofar as the simpler derivatives are concerned.

Among the general chemical properties of furan, the following may be listed as having a determinative influence on the technic of using it successfully: (1) Direct nitration of furan, unless carefully controlled, proceeds with explosive violence and yields only oxidation products. (2) Direct chlorination or bromination of furan leads to complex and uncontrollable reactions. (3) Substitution in the furan nucleus is always in the alpha-position unless both such positions are filled. (4) The alkyl furans—chloro-, bromo-, and iodofuran—are sensitive to the action of mineral acids; pyromucic acid, however, is stable, and it or its esters may be nitrated, sulfonated, chlorinated, or brominated readily. (5) The ready decarboxylation of pyromucic acid and many of its substitution products provides the readiest laboratory method for preparing such compounds as the halogenofurans and sulfonated furans. (6) Certain deriva-

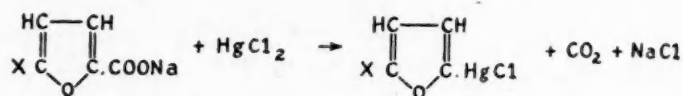
tives of tetrahydrofuran may be prepared by catalytic reduction of the corresponding furan compounds.

It has not been possible as yet to synthesize unsubstituted furan amines or compounds analogous to the phenols of benzene chemistry. There are indications, however, that an hydroxy compound may be formed as an intermediate product, although it has never been isolated (J.A.C.S., 58, 264, 1936). With the known furan amines, the diazo reaction takes an abnormal course (REC. TRAV. CHIM., 53, 13, 1934); consequently, in recent years, attention has been directed to the preparation of organo-metallic compounds as aids in synthesis.

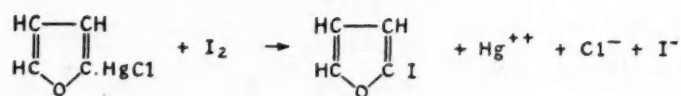
2-Chloromercurifuran is readily obtained by the action of an aqueous solution of mercuric chloride and sodium acetate on furan at room temperature, 2,5-dichloromercurifuran being formed at the same time:



2-Chloro-, 2-bromo-, and 2-nitrofuran do not undergo this reaction readily but may be prepared rapidly and in good yield by heating together an aqueous solution of the sodium salt of the corresponding acid and mercuric chloride:

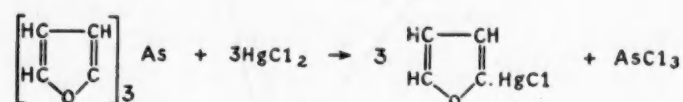


From these mercurials, the mercury is displaced by such reagents as acyl halides and the halogens, iodine causing scission of the carbon-mercury bond in boiling aqueous solution:



The carbon-mercury bond is transformed to a carbon-arsenic bond by the action of arsenic trichloride in benzene,

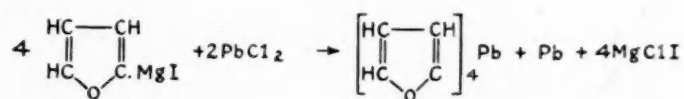
and back to the carbon-mercury bond by treatment of the arsenical in alcohol with mercuric chloride:



Substitution of arsenic by mercury has not been observed under these mild conditions in any other organic nucleus.

Of particular interest are the furan Grignard reagents which have been prepared recently (J.A.C.S., 54, 733, 1932; 52, 2083, 1930). The difficulties attendant upon their formation arise from the inertness of halogen in the furan nucleus. 2-Bromofuran forms a Grignard reagent with difficulty, but the reaction with 2-iodofuran goes smoothly. 3-Iodofuran, however, does not react with magnesium in a sealed tube at 150°, a temperature at which chlorobenzene forms a Grignard reagent readily.

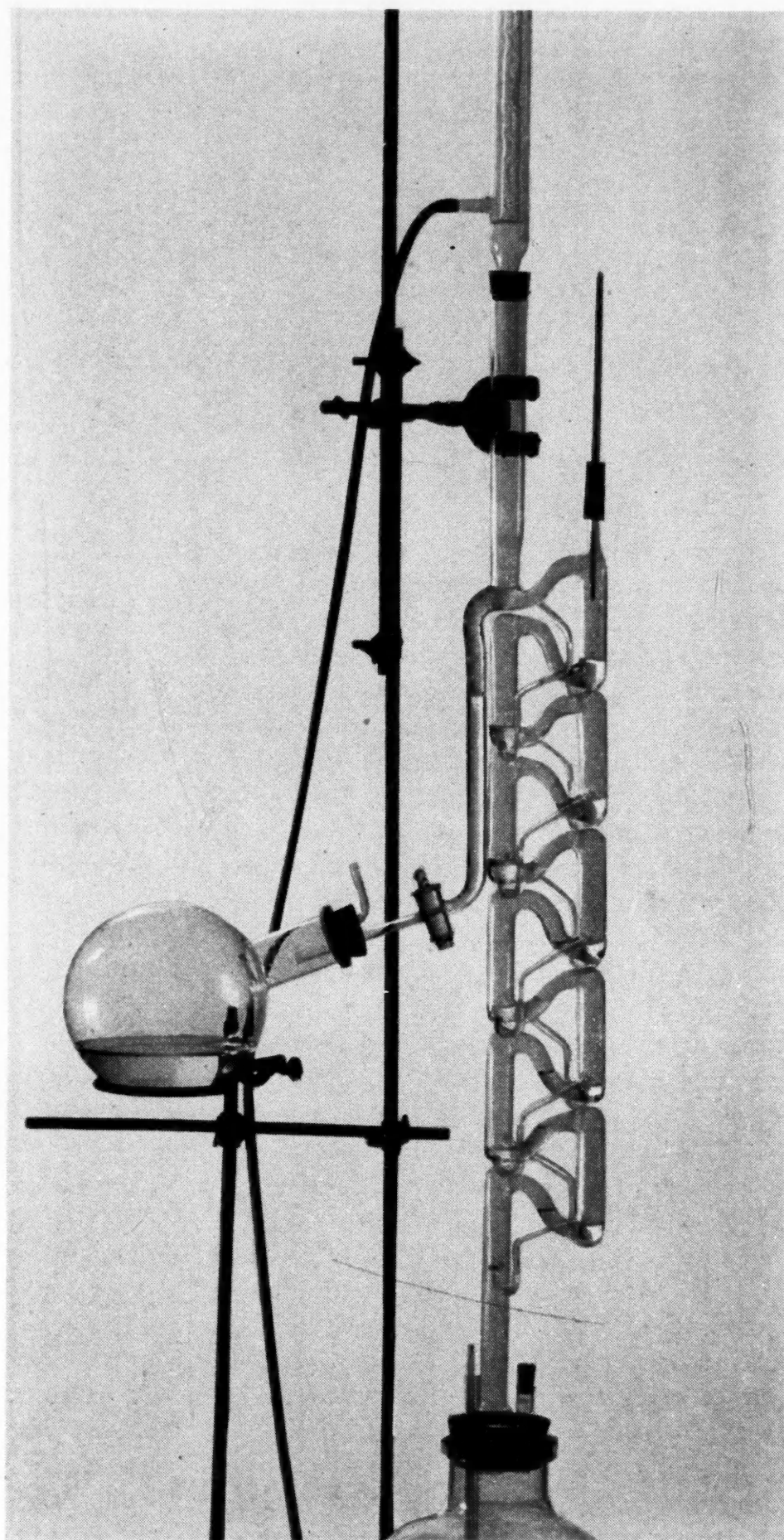
Furan-lead compounds may be prepared by the action of lead chloride on furan Grignard reagents:



Mixed compounds of this type, which contain, besides the furan nucleus, the benzene or the thiophene nucleus, have been prepared to show the selective scission of the furan nucleus by the action of strong mineral acids. It is possible to remove furan quantitatively from furyl-phenyl-lead in this way without breaking the benzene-lead bond. In the same way it has been shown that the furan-lead bond is more readily split than the thiophene-lead bond. A consideration of the relative reactivities of benzene, thiophene, and furan in this and certain other of the reactions most typical of aromatic compounds has given rise to the conception of superaromaticity in the furan series.

Preparation of Esters

THE Clarke and Rahrs distilling column has been slightly modified to facilitate its use in the preparation of esters or for the removal of water in other reactions. These changes are shown in the accompanying photograph. While the reaction mixture is being refluxed, the water collects in the side arm at the head of the distilling column. This tube may be graduated in order to show the rate of reaction and also to indicate when the process is complete. By means of the stopcock at the base of the tube, the water collected may be drawn off into a flask when necessary. When working with the higher alcohols, no water carrier is required, but with the lower alcohols, it is necessary to use benzene, toluene, xylene, etc. In cases where some alcohol collects with the water, the reaction is considered to be complete when the volume of alcoholic water in the side arm no longer increases. It is evident that the apparatus requires very little attention, as only an occasional glance will suffice to determine the progress of the reaction and its completion.



Modified Clarke and Rahrs column.

Eastman Organic Chemicals as Analytical Reagents

SINCE the inception of SYNTHETIC ORGANIC CHEMICALS, there have been presented in its pages many procedures employing organic chemicals for the detection, estimation, or determination of inorganic ions. These have been included with the hope that they would prove of interest and help to the many chemists who continually find need for a specific reagent to detect the presence or determine the concentration of a particular material.

An attempt has been made to present

this matter in as systematic a manner as possible, including, first, reagents for metallic ions; next, for the halogens; and eventually, for other ions. The first two subjects, while partially covered, can never be completed so long as research is continued. It is, therefore, the plan of the editors to deviate from the original schedule in order to include from time to time new methods appearing in the literature, which seem to have merit, as well as older methods which have not been presented previously.

XXXIX CADMIUM AND MOLYBDENUM

 α -BENZOINOXIME

H. B. Knowles, J. RESEARCH NATL. BUR. STAND., 9, 1 (1932)

Molybdenum in acid solution is precipitated quantitatively by α -benzoinoxime. The sample is dissolved in dilute sulfuric acid, and sulfurous acid added to reduce chromates or vanadates. To this solution are added 10 cc. of a 2% alcoholic α -benzoinoxime solution and 5 cc. extra for each 0.01 mg. of molybdenum present. Sufficient bromine water is added to color the solution and a few cc. additional reagent added. The precipitate is removed by filtration, washed with an α -benzoinoxime solution, dried carefully, and ignited to constant weight.

CYCLOHEXANOL

Hurd and Reynolds, IND. AND ENG. CHEM. (ANAL. ED.), 6, 477 (1934)

In the determination of molybdenum by the *James* method (Ind. and Eng. Chem., Anal. Ed., 4, 89) the metal is determined colorimetrically by extraction of the brown coloration produced by the formation of molybdenum thiocyanate. Cyclohexanol offers many advantages as the extractant. Smaller quantities are required to dissolve the thiocyanate, the color does not tend to

fade since the decomposition products of the solvent do not affect it, and the solvent may be easily recovered.

1-(2 QUINOLYL)-4-ALLYL THIOSEMICARBAZIDE

Scott and Adams, J.A.C.S., 57, 2541 (1935)

The reagent is prepared from 10 cc. of allyl iso thiocyanate and 16 grams of 2-quinolyldiazine in ether. A saturated solution of the reagent (0.05 gm. in 100 cc.) in 50% alcohol is added to a solution of cadmium nitrate containing iodides. A bright greenish-yellow precipitate is formed even with traces. Copper, if present, is precipitated with potassium iodide. The reagent then is added and the yellow cadmium thiosemicarbazide precipitates. The copper precipitate is dissolved by the addition of ammonium hydroxide, but the cadmium complex remains.

Increase in Price

Added cost of raw materials necessitates the following price increase. See page 64 List No. 27 "Eastman Organic Chemicals."

679 Levulose 100 g. \$3.80 C